UCB009-CHEMISTRY

THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

Infra-red (IR) spectroscopy (Vibrational Transitions)

A brief outline of IR spectroscopy:

➢ Introduction to IR radiation

➢ Molecular vibrations and modes

➢ Hooke's law: reduced mass and force constant

➢ Factors affecting the vibrational frequency

➢ Principle of IR spectroscopy

➢ Criteria for a molecule to absorb IR radiation

➢ Classification of vibrational transitions in molecules

➢ Features of an IR spectrum

➢ Relationship between wavelength and wavenumber

➢ Why the x-axis of an IR spectrum is expressed in wavenumber

➢ Why does the IR spectrum contain inverted peaks

➢ Vibrational degrees of freedom

➢ IR spectra of CO_2 and H_2O

➢ Regions in the IR spectrum and their significance

➢ Distinguish between intramolecular and intermolecular hydrogen bonding
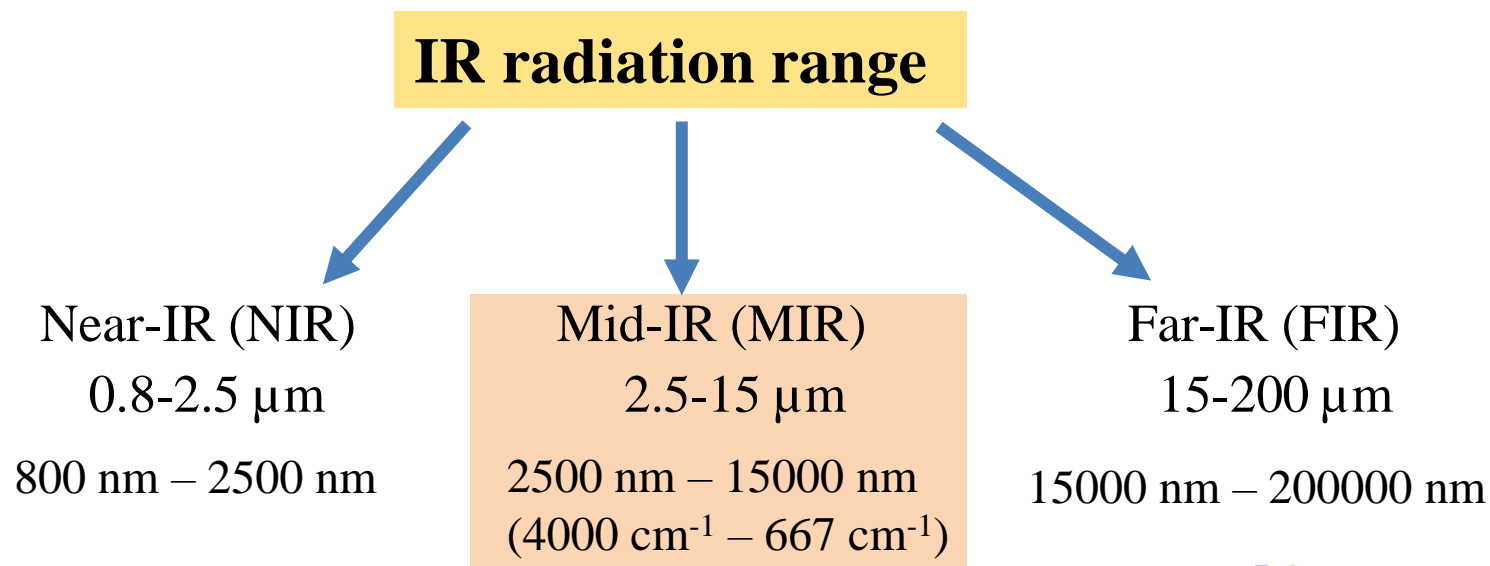
➢ Application of IR

Introduction to IR Radiation:

➤ The light our eyes see is a small part of a broad spectrum of electromagnetic radiation.

➤ On the immediate high energy side of the visible spectrum lies the ultraviolet, and on the low energy side is the infrared.
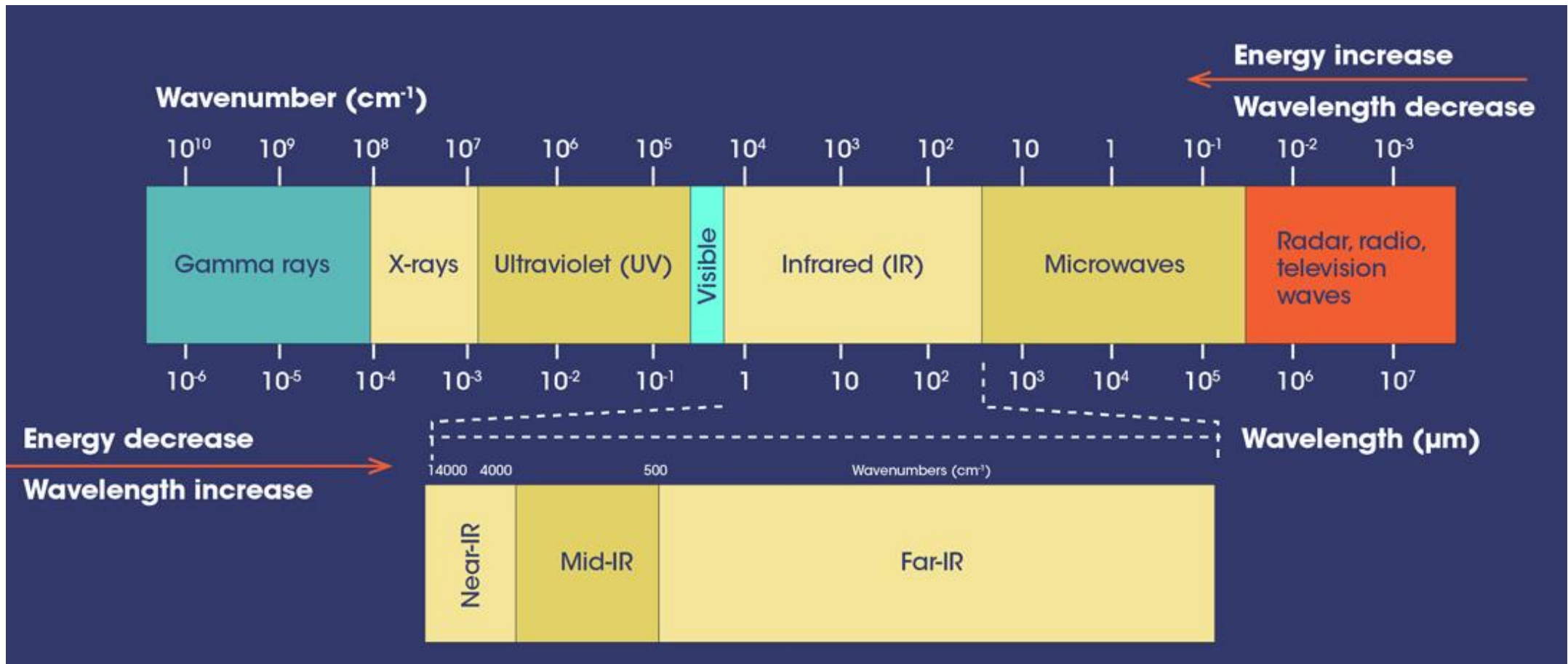
Introduction to IR Radiation:

The portion of the infrared region **most useful** for the **analysis of organic compounds** is the **mid-IR** region that is not adjacent to the visible radiation.

IR radiation range

| Near-IR (NIR)	Mid-IR (MIR)	Far-IR (FIR)
0.8-2.5 μm	2.5-15 μm	15-200 μm
800 nm – 2500 nm	2500 nm – 15000 nm ($4000\ cm^{-1}$ – $667\ cm^{-1}$)	15000 nm – 200000 nm

Note: Energy associated with the infrared region is sufficient enough to cause vibrational transitions only (i.e., molecules get vibrated), not the electronic transitions in the molecules.

Recall: The electronic transition occurs due to the photons in the UV-visible region.

E=2

v'=2
v'=1
v'=0

E=1

Electronic transitions
(UV-Vis radiation required)

v''=2
v''=1

Vibrational transitions
(IR radiation required)

v''=0

E=0
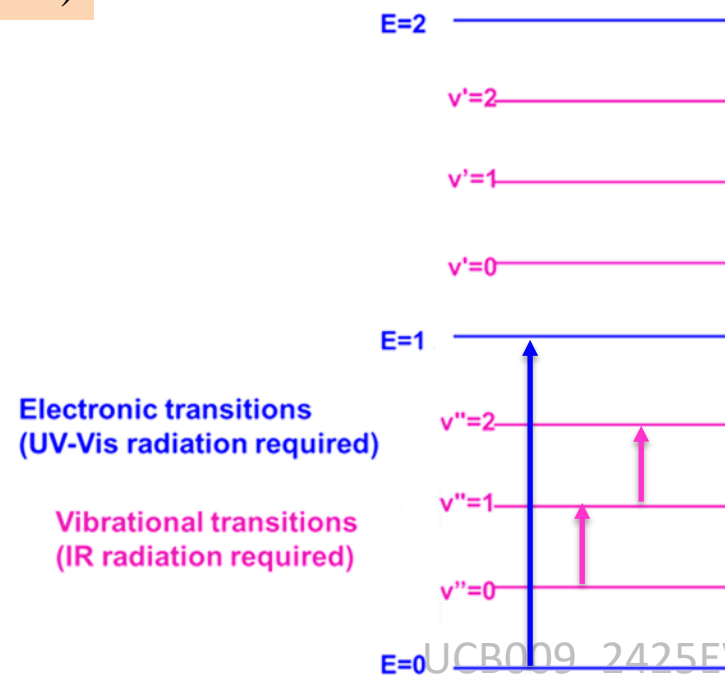
Why do molecules vibrate?

- An organic molecule consists of covalent bonds between atoms.

- Every covalent bond can be assumed as a spring holding the atoms together.

- A spring (i.e. a chemical bond) can undergo both stretching and compression

- IR radiation induces vibrational transitions in molecules.

Equilibrium bond length

Compressed covalent bond

Stretched covalent bond
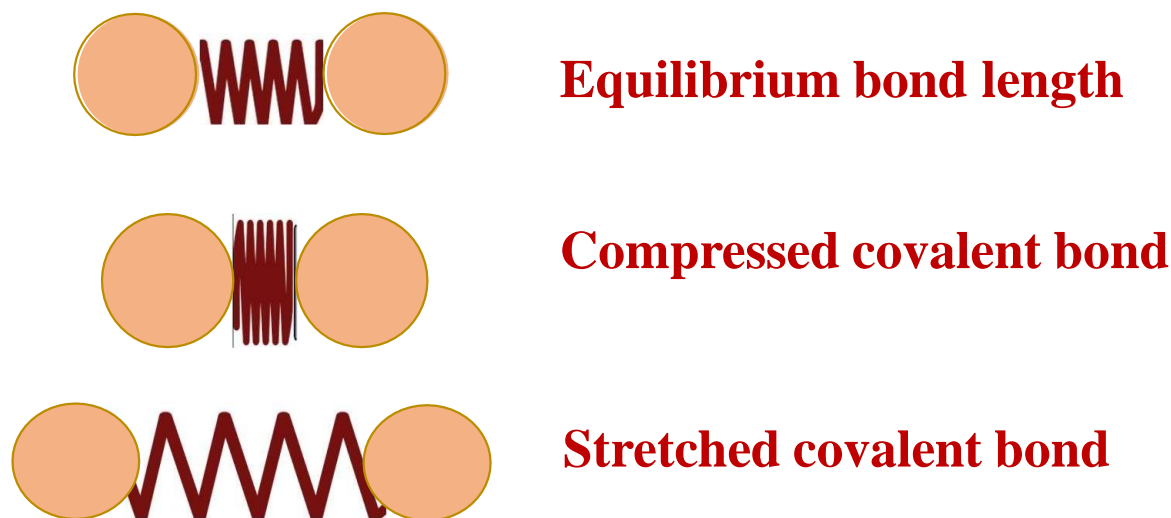
Note: All molecules are not diatomic; they can be triatomic or polyatomic too.

Exercise 1:
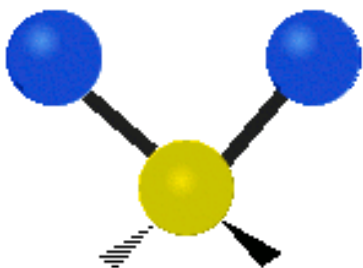True or False: Sodium chloride and Potassium chloride will vibrate

What are molecular vibrations?
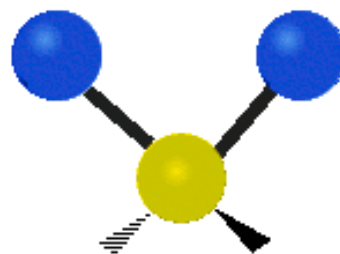
Modes of Vibration:

1- Stretching Vibrations

2- Bending vibrations

A- In-plane bending

Symmetric stretching
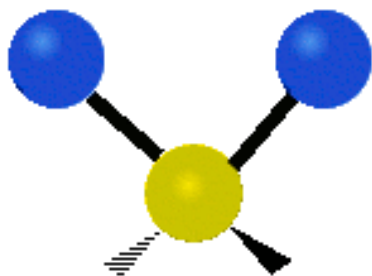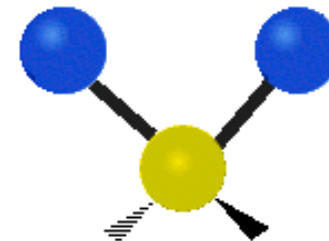
Scissoring

Rocking

b- Out-of-plane bending

Asymmetric stretching

Twisting

Wagging

Energy order: Asymmetric > Symmetric > bending for IR absorption
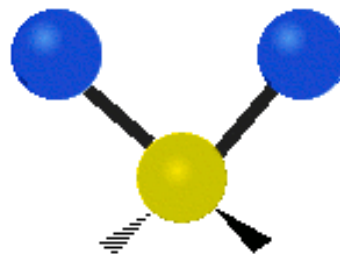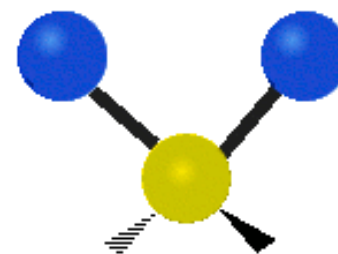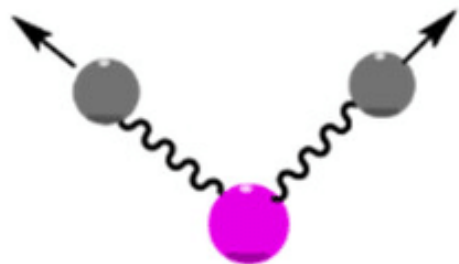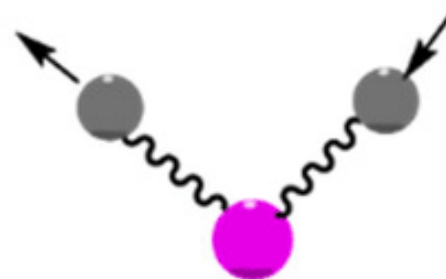
Modes of Vibration: Another representation of directional bond movements
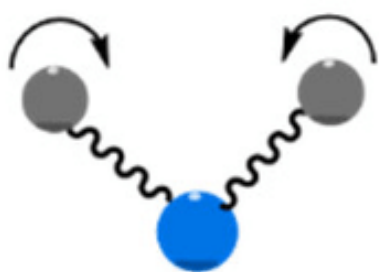
Stretching Vibrations
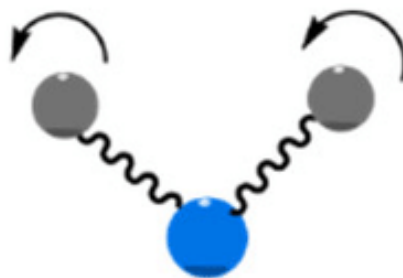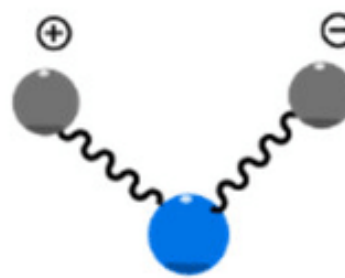

Symmetrical

Asymmetrical
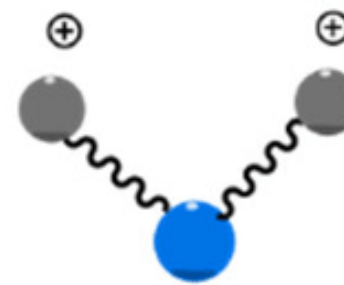
Bending Vibrations

Scissoring

Rocking

Twisting

Wagging

In plane

Out of plane

Do all covalent bonds vibrate at the same frequency?

➢ Recall: All covalent bonds can be assumed as springs holding the atoms together.

   Note: The molecule may have more than one type of covalent bond.

➢ During molecular vibrations, the atoms/nuclei of a molecule change their relative positions whereas, the center of mass of the molecule does not change.

➢ These vibrations can be modeled as harmonic oscillators, where the restoring force (F) is proportional to displacement as per **Hooke's Law**

$$F = -kx \quad or \quad E = \frac{1}{2}kx^2$$

where k: force or spring constant

   x: displacement

   E: potential energy
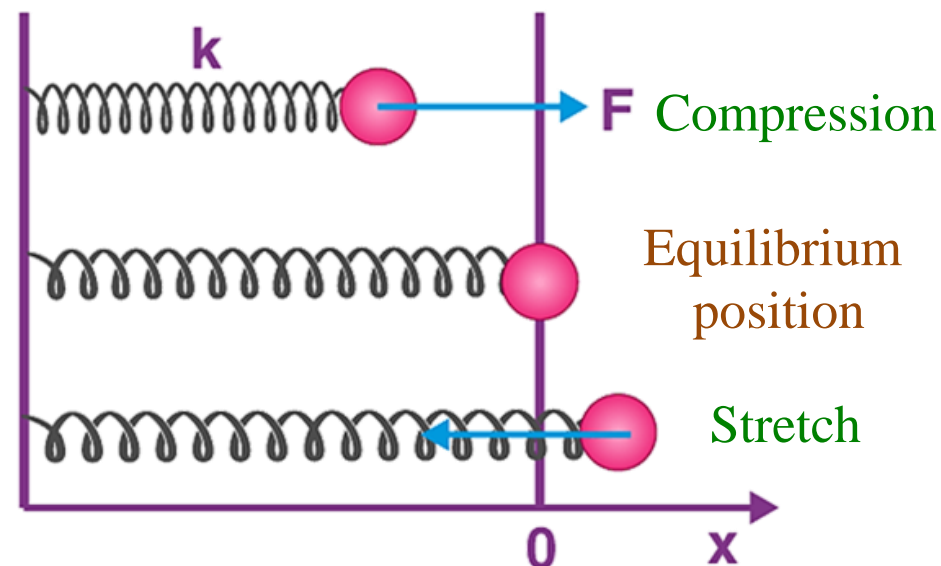
➢ The *negative* sign denotes that the directions of the restoring force (F) and the displacement (x) vectors are opposite to each other.

➢ Hence, the energy (E) required to either stretch or compress a given bond in a molecule is equal/same.

Do all covalent bonds vibrate at the same frequency?

Therefore, based on a simple harmonic oscillator model, the classical vibrational frequency of a covalent bond can be estimated from **Hooke's law** as:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \; Hz \qquad \text{or} \qquad \bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \; cm^{-1}$$

Where:

ν = vibrational frequency (Hz)

k = force constant (Nm^{-1} or dynes/cm)

μ = reduced mass (kg)

Where:

$\bar{\nu}$ = wavenumber (cm^{-1})

c = speed of light (3×10^{10} cm/s)

$$\mu = \frac{M_1 \times M_2}{M_1 + M_2}$$

M$_1$ & M$_2$ = masses of atoms in kg

Note: Fundamental vibrational frequencies are ALWAYS expressed in cm^{-1}

Factors affecting the vibrational frequency:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \ Hz \qquad \text{or} \qquad \bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \ cm^{-1}$$

If Bond strength (k) increases
or
Reduced mass (μ) decreases

vibrational frequency increases

If Bond Strength (k) decreases
or
Reduced mass (μ) increases

vibrational frequency decreases

Effect of force constant on vibrational frequency:

1. Force constant when both atoms are same (reduced mass is same)

Bond	Force constant (dynes/cm)	Vibrational frequency (cm^{-1})
C−C	5×10^5	~1100 cm^{-1}
C=C	10×10^5	~1650 cm^{-1}
C≡C	15×10^5	~2200 cm^{-1}

2. Force constant when both atoms are different (when reduced mass is almost similar):

Bond	Force constant (dynes/cm)	Vibrational frequency (cm^{-1})
C−H	4.69×10^5	~2900 cm^{-1}
O−H	6.12×10^5	~3600 cm^{-1}

Exercise 2:

For the following set of covalent bonds, which one has a higher vibrational frequency
- C-C vs C=C
- C-H vs C-D
- C-N vs C≡N

Hints to solve this exercise:
- Take a critical look at the bond type
- Recall the various parameters in Hooke's law
- Think how is the vibrational frequency related to these parameters

Exercise 3:

(a) Rank the following bonds in order of increasing stretching frequency (cm^{-1}) in IR spectroscopy:
O-H, C≡N, C-N and C=O
(b) Why C=O stretching occurs at higher frequencies than the stretching of C=C bond?

Hints to solve this exercise:
- Take a critical look at the bond type
- Recall the various parameters in Hooke's law
- Arrange them in an increasing order (i.e. from lower to higher) vibrational frequency

Exercise 4:

(a) Calculate the approximate stretching frequency of C-H (cm^{-1}) from the following data:
$k = 500$ Nm^{-1}, $m_C = 20$ X 10^{-24} g, $m_H = 1.6$ X 10^{-24} g. (Ans: 3084 cm^{-1})

(b) ^1H ^{35}Cl gas has a force constant (k) value of 480 N/m. Calculate the fundamental frequency (in Hz) and its wavenumber (cm^{-1}). (Ans: 8.66×10^{13} Hz, 2888 cm^{-1})

Hints to solve this exercise:

- At first, see whether the masses of the given atoms are in atomic mass units (a.m.u. i.e. atomic masses only)
- If given in a.m.u., first convert them into kg using the conversion formula: 1 a.m.u. = 1.66 x 10^{-27} kg
- If the masses are already provided in grams; convert them into kg.
- Calculate the reduced mass of the given covalent bond in kg.
- Apply Hooke's law and calculate the vibrational frequency in Hertz (Hz) using given parameters.
- **Very Important Step:** Convert the vibrational frequency (in Hz) into wavenumber (cm-1) by applying another formula (shown earlier).

Principle of IR spectroscopy:

A molecule will absorb IR radiation when the natural frequency of vibrations of bond(s) of a molecule is the same as that of the frequency of incident radiation.
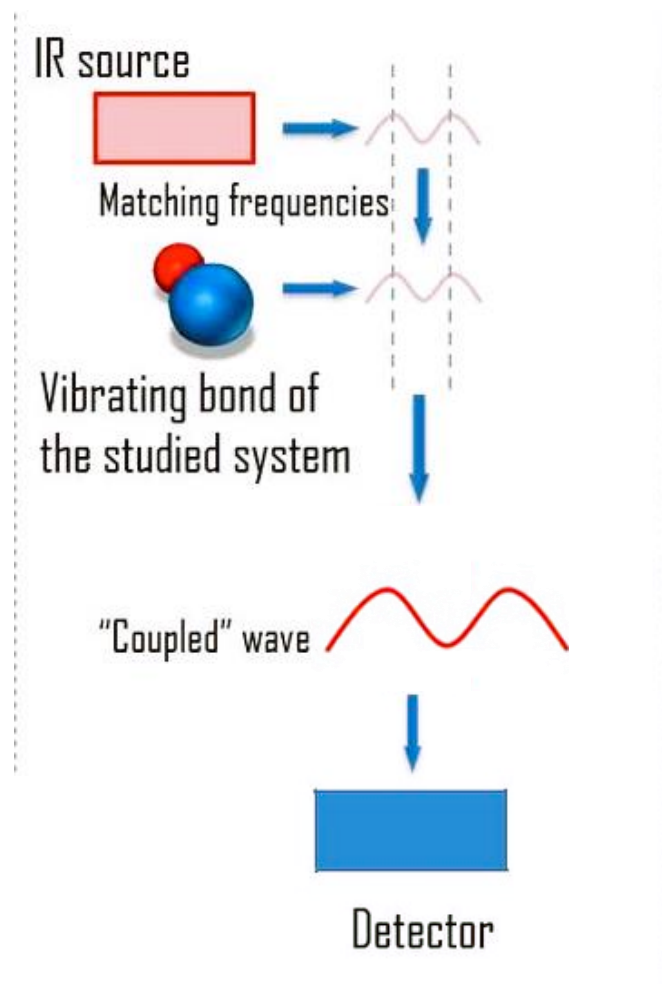
Criteria for a molecule to absorb IR radiation

Changes/fluctuations in the dipole moment

A molecule is said to have a dipole moment when there is a separation of charge between two atoms in a covalent bond.
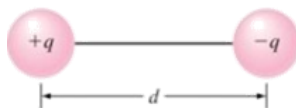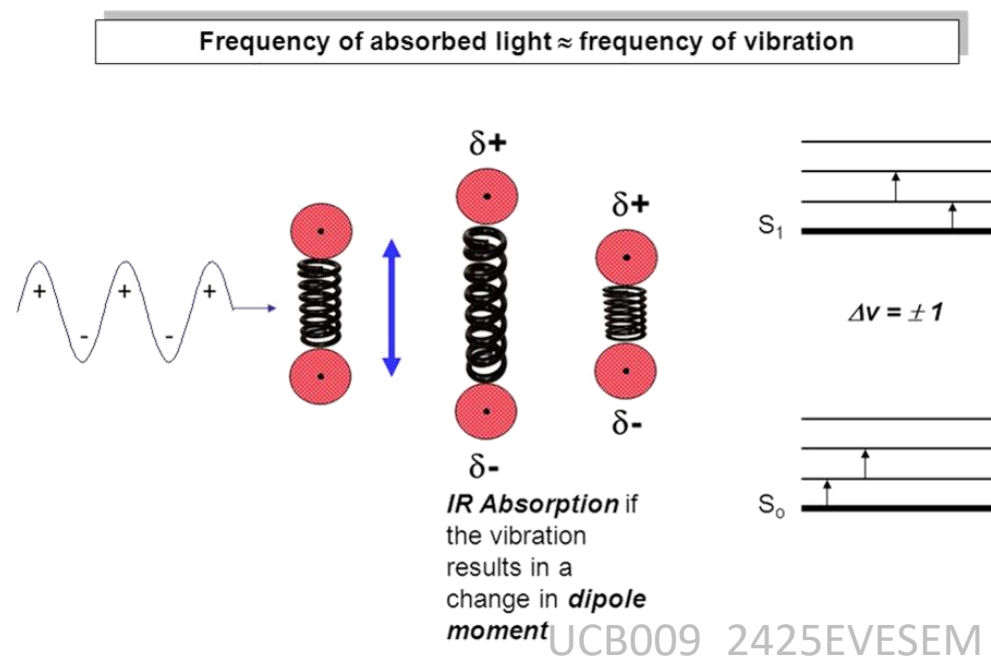
Dipole moment   Dipole moment of a bond in a molecule

The vibrational motion of the molecule should be accompanied by a change in (fluctuating) dipole moment, i.e., the dipole moment must change during the vibration.

Why is the fluctuating dipole moment important for IR absorption?

- ➤ As the bond vibrates, the distance between the charges increases and decreases, so the dipole moment also oscillates back and forth
- ➤ Thus, IR radiation can interact with the oscillating dipole.
- ➤ If the IR radiation has the same frequency as the oscillating dipole, the IR photons will be absorbed by the molecule
- ➤ Vibrational transitions will occur
- ➤ We obtain an IR spectrum of the molecule

Frequency of absorbed light ≈ frequency of vibration

$\delta+$

$\delta+$

$\delta-$

$\delta-$

S_1

$\Delta v = \pm 1$

S_0

IR Absorption if the vibration results in a change in **dipole moment**

Classification of Vibrational Transitions in Molecules

Vibrational transitions

IR active transitions

- a significant change in the dipole moment of a chemical bond
- leads to strong absorption bands **e.g.** Carbonyl group
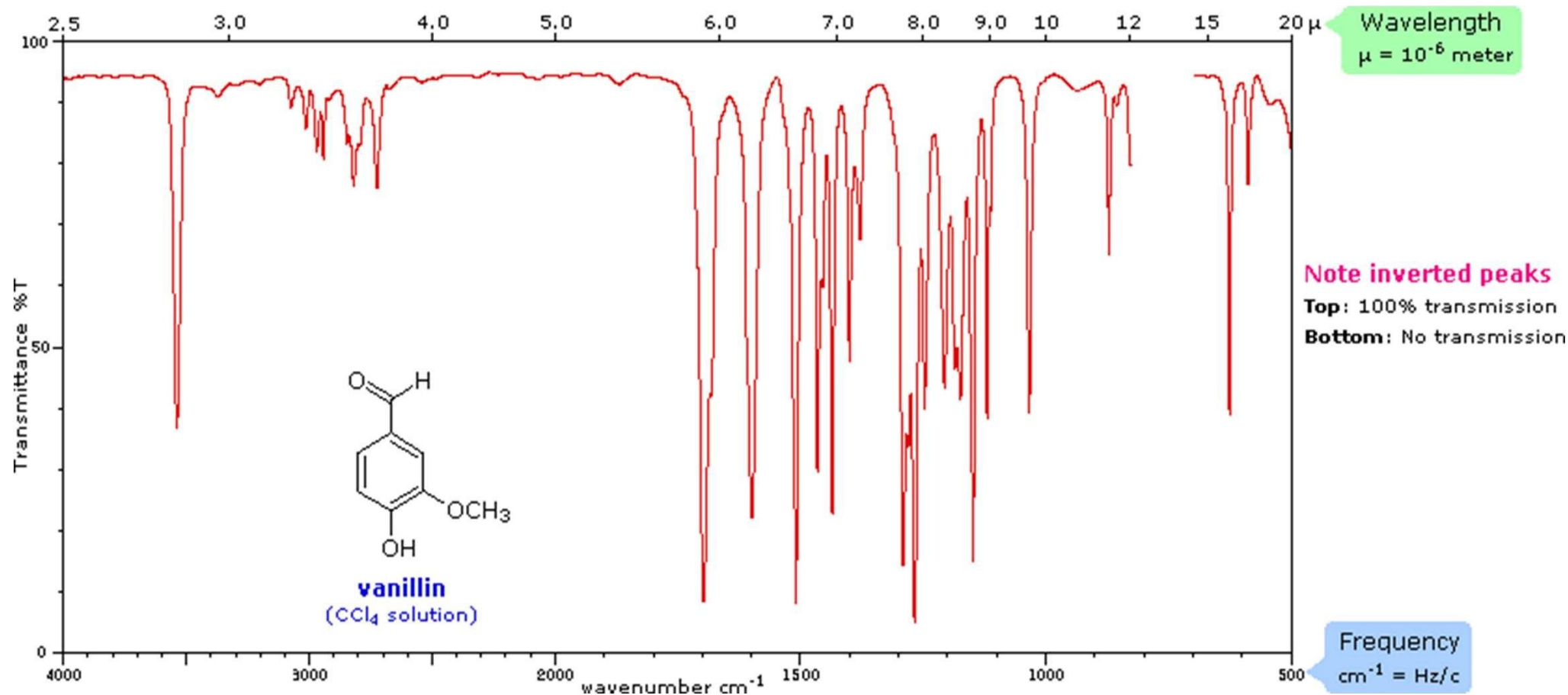
IR inactive transitions

- do not result in any change in the dipole moment
- does not give rise to any absorption band **e.g.**, Homonuclear diatomic molecules

Exercise 5:

Find out which of the following molecules are IR active and IR inactive

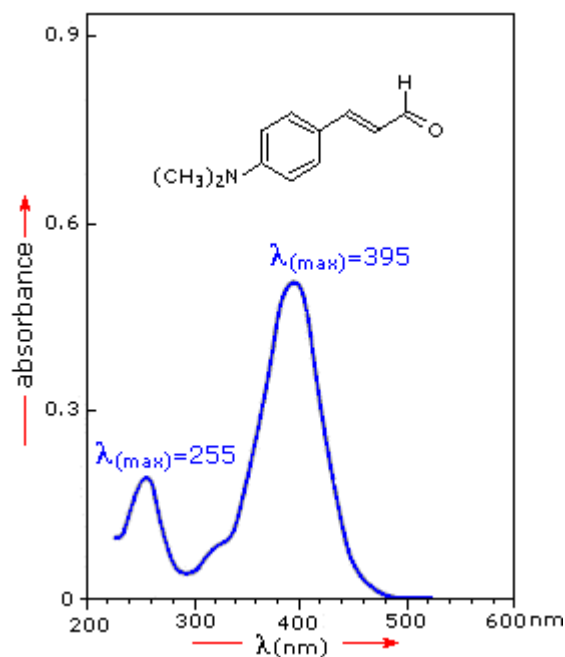(i) H_2 (ii) CO (iii) H_2O (iv) CO_2 (v) SO_2 (vi) Benzene

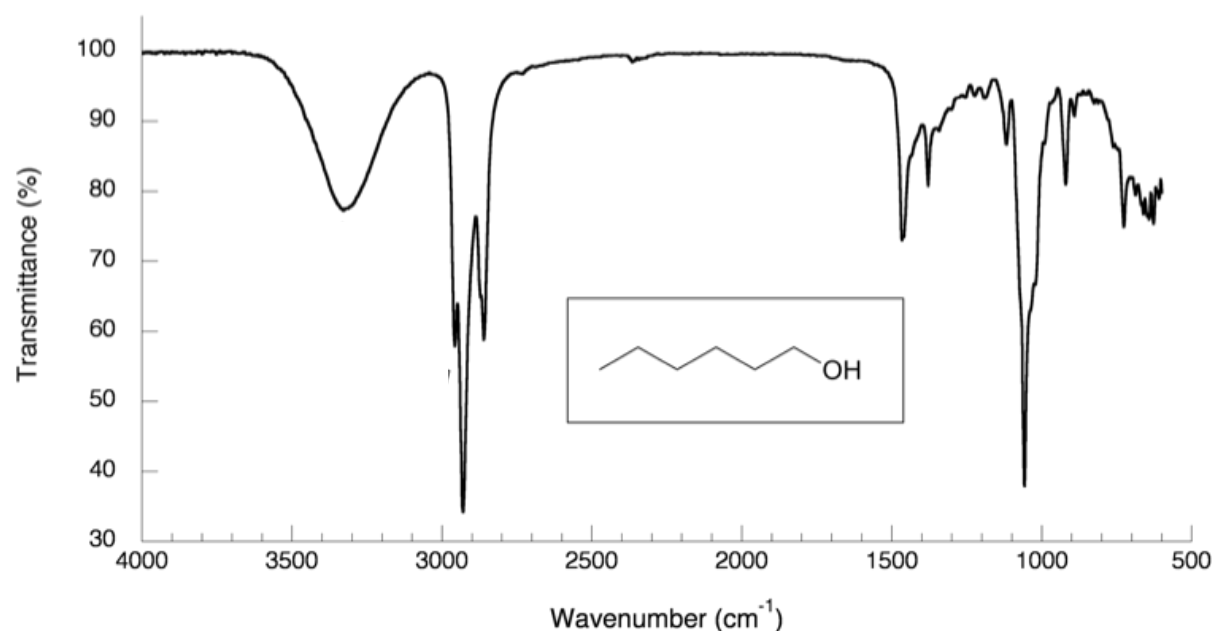# What does an Infra-red (IR) spectrum look like:

Exercise 6:

Spot the differences between the following spectra

UV-Vis

IR

Hints to solve this exercise:

➤ Look for the labels on the x-and y-axes

➤ Identify the directions of the peaks

 ➤ **Why the x-axis of an IR spectrum is expressed in wavenumber?**

 ➤ **Why the y-axis of an IR spectrum is expressed in percent transmittance?**
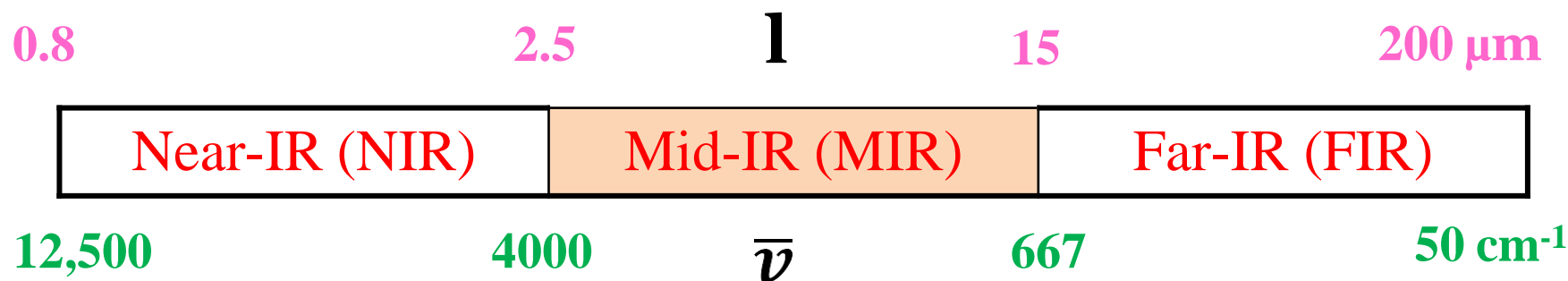
Relationship between Wavelength and Wavenumber

Absorption of IR radiations can be expressed in terms of either wavelength or **wavenumber $(\overline{v})$** – *preferred*

$$c = v\lambda \implies \frac{v}{c} = \frac{1}{\lambda} \qquad \frac{v}{c} = \overline{v}\,(cm^{-1}) = \frac{1}{wavelength\,(cm)} = \frac{1}{\lambda}$$

e.g. $\quad 1\ \mu m = 10^{-6}\,m = 10^{-6} \times 10^2\,cm = 10^{-4}\,cm$

Hence, $15\ \mu m = 15 \times 10^{-4}\,cm$

$$\overline{v}\,(cm^{-1}) = \frac{10000}{wavelength\,(\mu m)}$$

0.8		2.5	l	15	200 μm
	Near-IR (NIR)		Mid-IR (MIR)		Far-IR (FIR)
12,500		4000	$\overline{v}$	667	50 cm⁻¹

Note: IR spectrum is recorded as back-to-front (i.e. from lower energy to higher energy)

Recall: Energy $(E) \propto {}^1/_\lambda = \overline{v} \implies E \propto \overline{v}$ Hence, if $\overline{v} \uparrow$ then, $E \uparrow$ and vice-versa

# Why the x-axis of an IR spectrum is expressed in wavenumber?

As the gaps between the vibrational energy levels are very less compared to that of the electronic energy levels, sometimes it becomes difficult to differentiate between two closest peaks on the wavelength scale.

However, the differentiation becomes more clear if we express the wavelength in wavenumber.
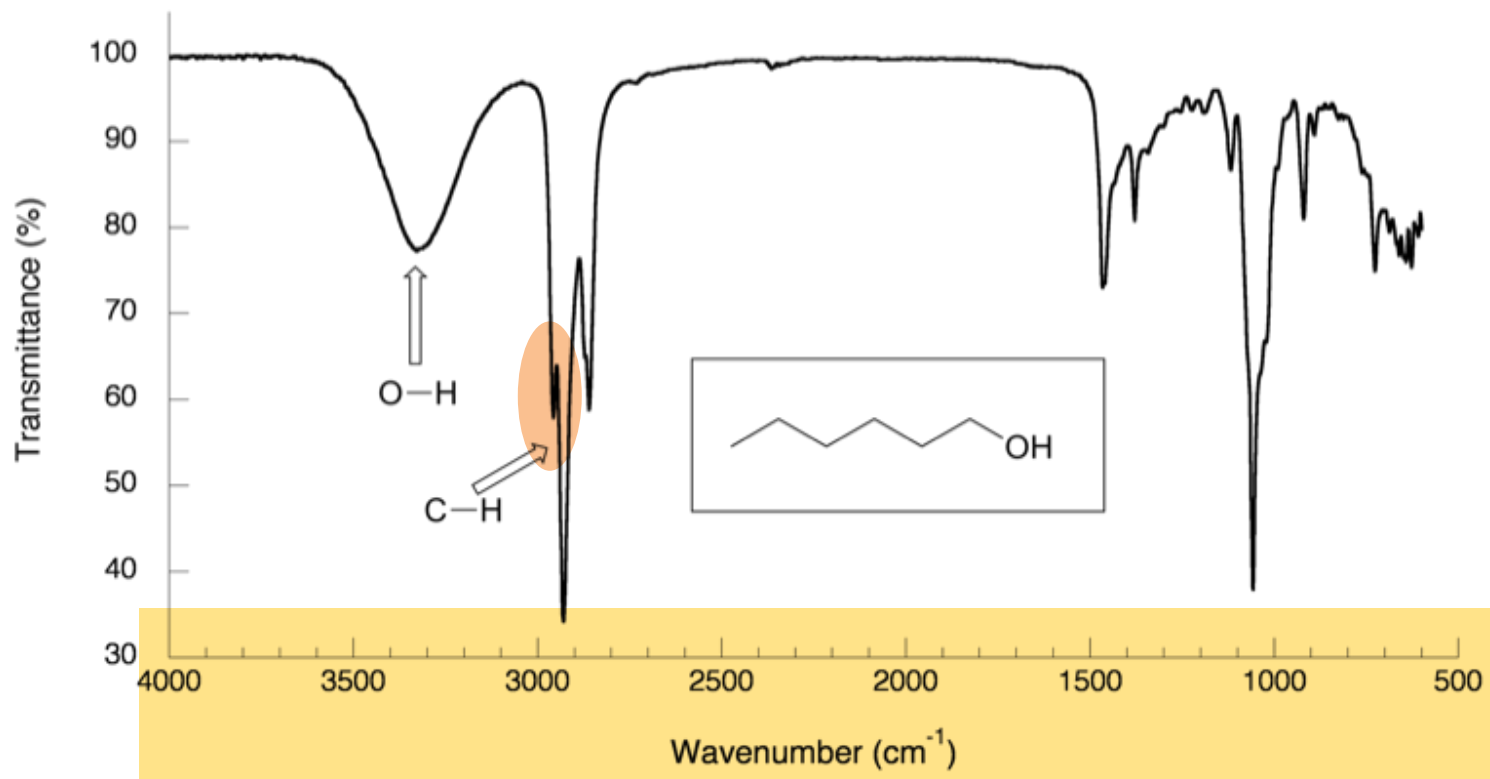
- E.g., if one band occurs at 3000 cm^{-1} and another band occurs at 2990 cm^{-1} (both circled in orange color in the spectrum), then we can easily say that the two bands are 10 cm^{-1} apart from each other.

- But, if we convert these wavenumbers into wavelengths,

  - the band (3000 cm^{-1}) will occur at 3.333 μm and

  - another band (2990 cm^{-1}) will occur at 3.344 μm.

  - Hence, on the wavelength scale, both bands are 0.011 μm apart from each other.

- Imagining 10 cm^{-1} difference is more convenient than 0.011 μm difference.

Why the y-axis of an IR spectrum is expressed in percent transmittance? Or why does the IR spectrum contain inverted peaks?
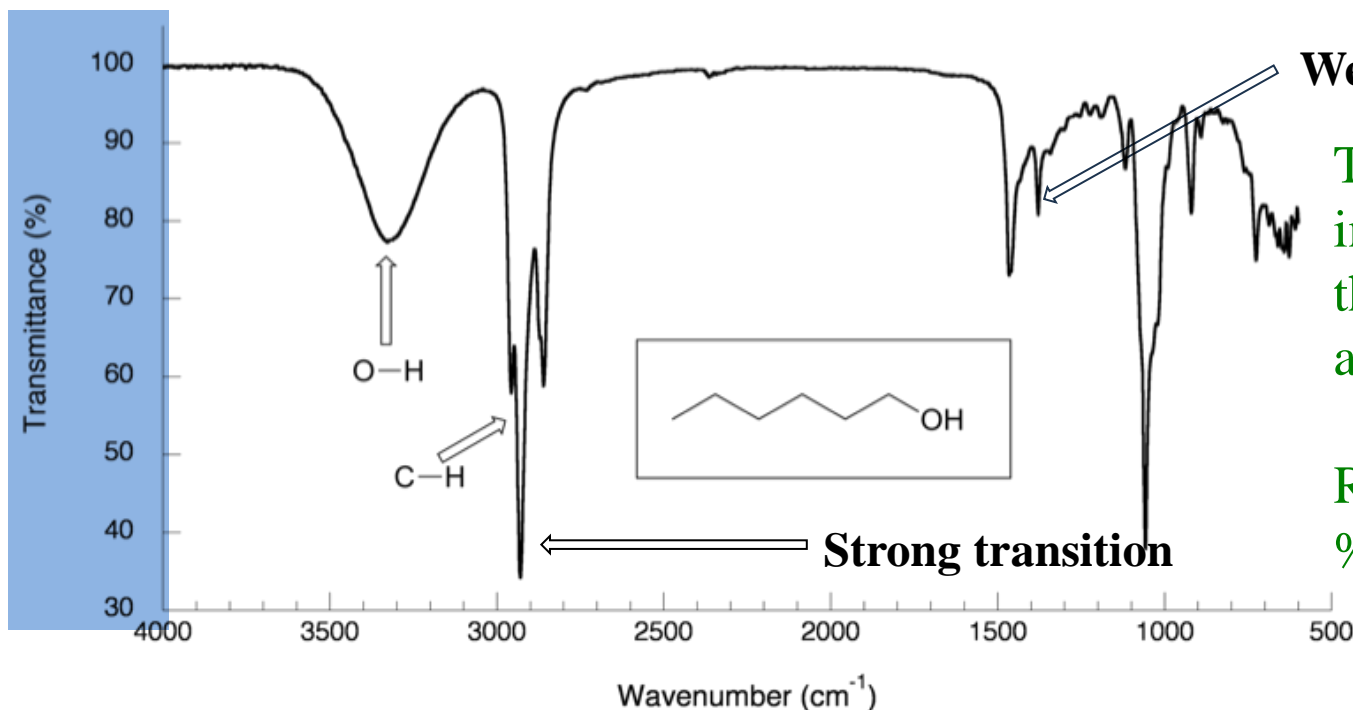
Weak transition

Transmittance is the fraction of incident infrared radiation that passes through a sample without being absorbed

Recall $A = \log(1/T)$

% Absorption = 100 - % Transmittance

Strong transition

The main advantage of the percent transmittance mode:

➤ Weak vibrational transitions mean a lesser amount of IR radiation is absorbed

- implies the extent of absorption is very less
- implies transmittance of IR radiation is very high

➤ Hence, in an IR spectrum, the weaker transitions are not masked by intense, stronger transitions.

Note: IR spectrum is conventionally recorded in transmittance, but it may be recorded in absorbance mode too

Vibrational Degrees of Freedom: Number of All Possible Vibrations

Degrees of Freedom: The number of independent ways in which an atom or a molecule can exhibit motion is called degrees of freedom

3D space coordinates
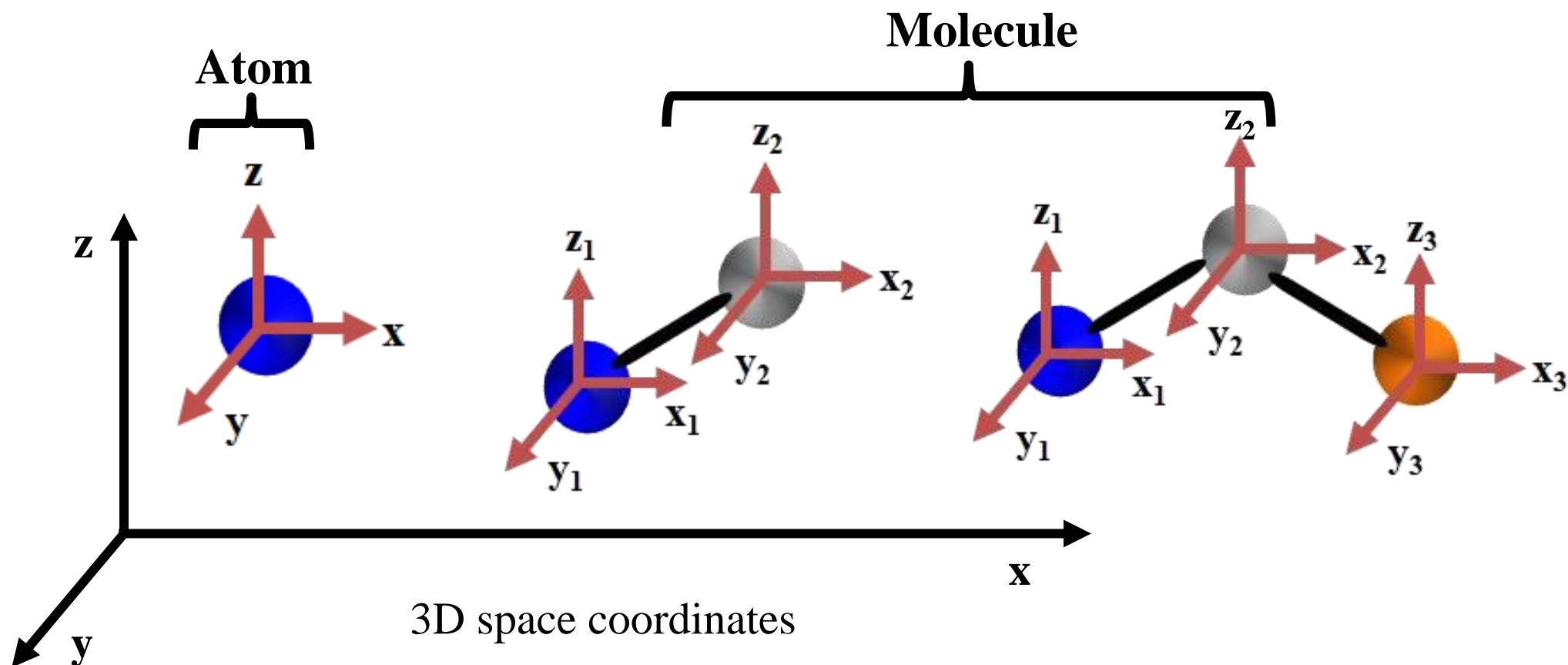
If a molecule has N number of atoms
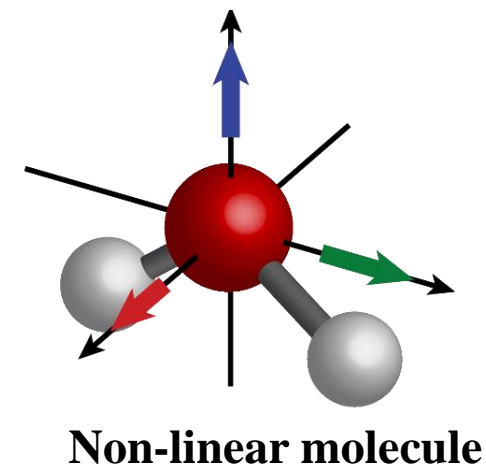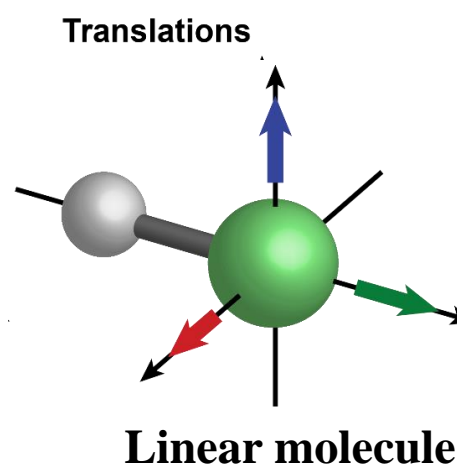
∴ its **TOTAL** degrees of freedom = **3N**

Total degrees of freedom (3N) = Translational + Rotational + Vibrational

∴ **Vibrational degrees of freedom = Total − (Translational + Rotational)**

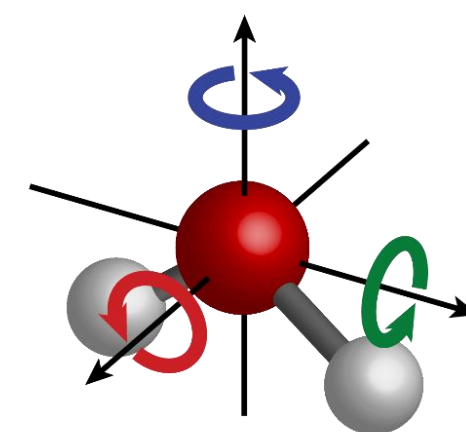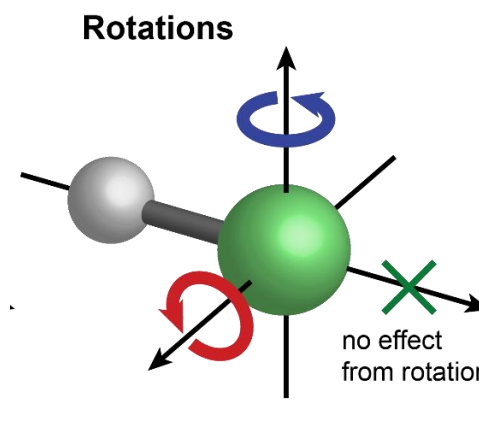# Vibrational Degrees of Freedom: Number of All Possible Vibrations

➢ Translational degrees of freedom:

❖ involve translational movements of the entire molecule in one of the three orthogonal directions

❖ **Translational degrees of freedom = 3**

(irrespective of the shape of the molecule)

➢ Rotational degrees of freedom:

❖ **LINEAR** molecule (e.g. HCl) can rotate around two separate axes that are perpendicular to the bond

❖ **Rotational degrees of freedom = 2**

❖ **NON-LINEAR** molecule (e.g. H_2O) can rotate around 3 perpendicular axes.

❖ **Rotational degrees of freedom = 3**

➢ Vibrational degrees of freedom =

Total − (Translational + Rotational)

i.e.   3N − (Translational + Rotational)

Translations

Linear molecule   **Non-linear molecule**

Rotations

no effect from rotation

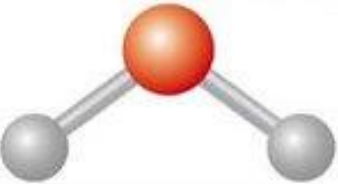Translational and rotational degrees of freedom of HCl (left) and water (right).

Linear molecules	Non-linear molecules
$3N - 5$	$3N - 6$

Vibrational Degrees of Freedom for Various Molecules

Type of molecule	N	Degrees of freedom	Modes
Monatomic, e.g. Ne	1	3	3 translational 0 rotational 0 vibrational
Diatomic, e.g. HCl	2	6	3 translational 2 rotational 1 vibrational
Triatomic linear, e.g. CO_2	3	9	3 translational 2 rotational 4 vibrational
Triatomic non-linear, e.g. H_2O	3	9	3 translational 3 rotational 3 vibrational

Note: These are theoretically calculated total number of all possible vibrations
          But the actual number of vibrational bands, visible in an IR spectrum, may vary in reality.

Exercise 7:

Calculate the number of vibrational degrees of freedom for the following molecules
Carbon dioxide, Water, Benzene, Toluene, Acetylene

Vibrational degrees of freedom =
Total – (Translational + Rotational)
i.e.   3N – (Translational + Rotational)

Linear molecules	Non-linear molecules
$3N - 5$	$3N - 6$

| Molecule	Number of atoms	Total DoF	Translational DoF	Rotational DoF	Vibrational DoF
Carbon dioxide	3	3n = 3 x 3 = 9	3	2	9 – 5 = 4
Water	3	3n = 3 x 3 = 9	3	3	9 - 6 = 3
Benzene	12	3n = 3 x 12 = 36	3	3	36 – 6 = 30
Toluene	15	3n = 3 x 15 = 45	3	3	45 – 6 = 39
Acetylene	4	3n = 3 x 4 = 12	3	2	12 – 5 = 7

Note: These are theoretically calculated total number of all possible vibrations
But the actual number of vibrational bands, visible in an IR spectrum, may vary in reality.

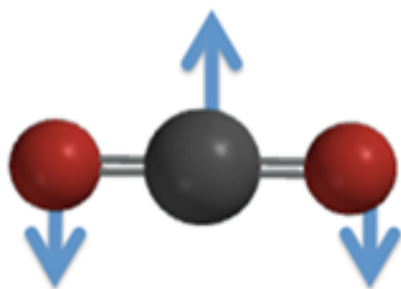# Vibrational Modes of Carbon Dioxide (CO_2)

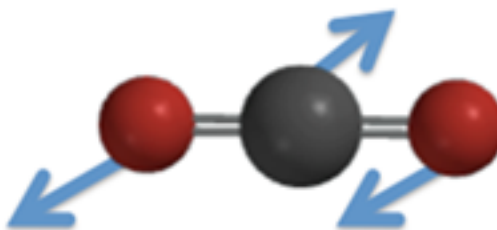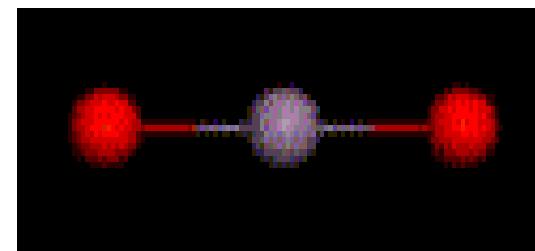Number of theoretically possible vibrational modes = $3n - 5 = 3 \times 3 - 5 = 4$
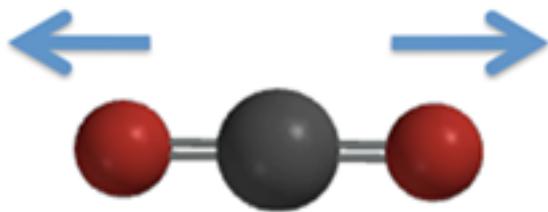
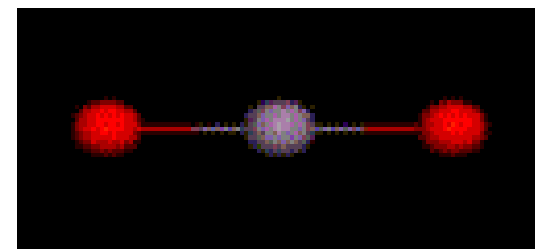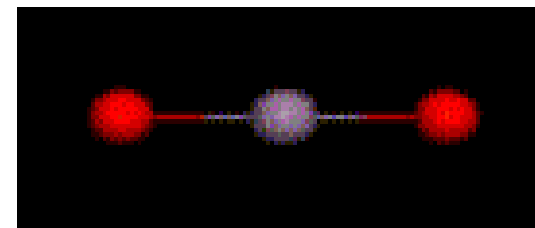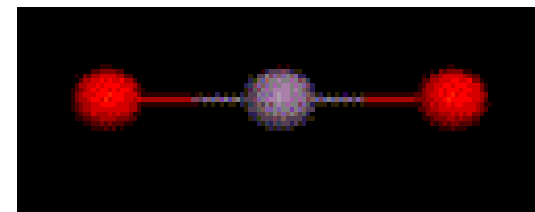Symmetric Stretching
(Not IR active)
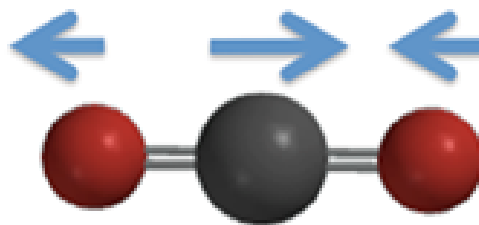
Asymmetric Stretching
(IR active)

Vertical Bending
(IR active)

Horizontal Bending
(IR active)

IR Spectrum of CO$_2$
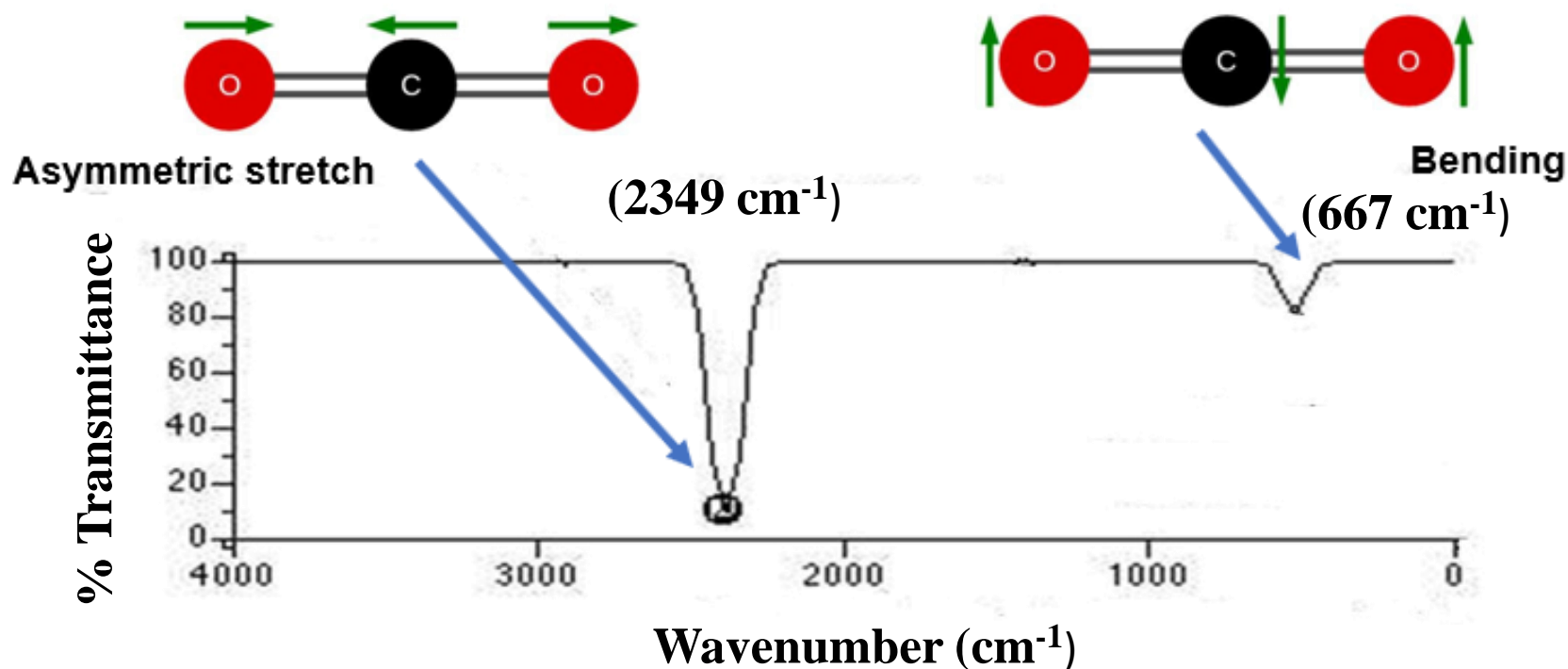
Number of bands visible/present in the IR spectrum = 2

One is due to asymmetric stretch and the other is due to bending vibrations

Note: Since both bending modes are of equal energy, hence, they overlap and show only 1 band instead of 2 separate bands

Exercise 8:

Identify the higher energy vibrational mode in the IR spectrum of CO$_2$ shown above
Hint: Recall the relationship between Energy (E) and Wavenumber ($\bar{v}$)

Vibrational Modes of Water (H_2O)

Number of theoretically possible vibrational modes = $3n - 6 = 3 \times 3 - 6 = 3$
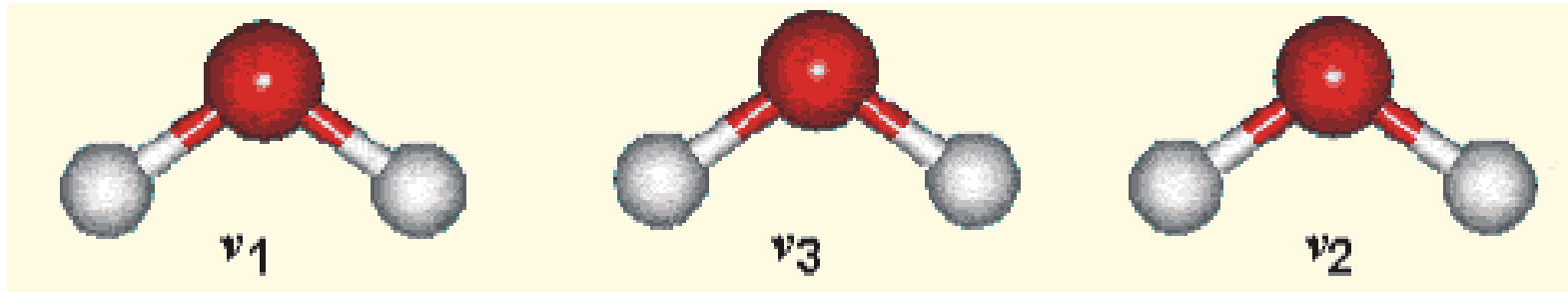
| Symmetric Stretching (IR active) | Asymmetric Stretching (IR active) | Bending (IR active) |

IR spectrum of H_2O:

O-H Bending
(1750-1500 cm-1)

O-H Stretching
(3550-3200 cm-1)

Transmittance

Wavenumber (cm^{-1})
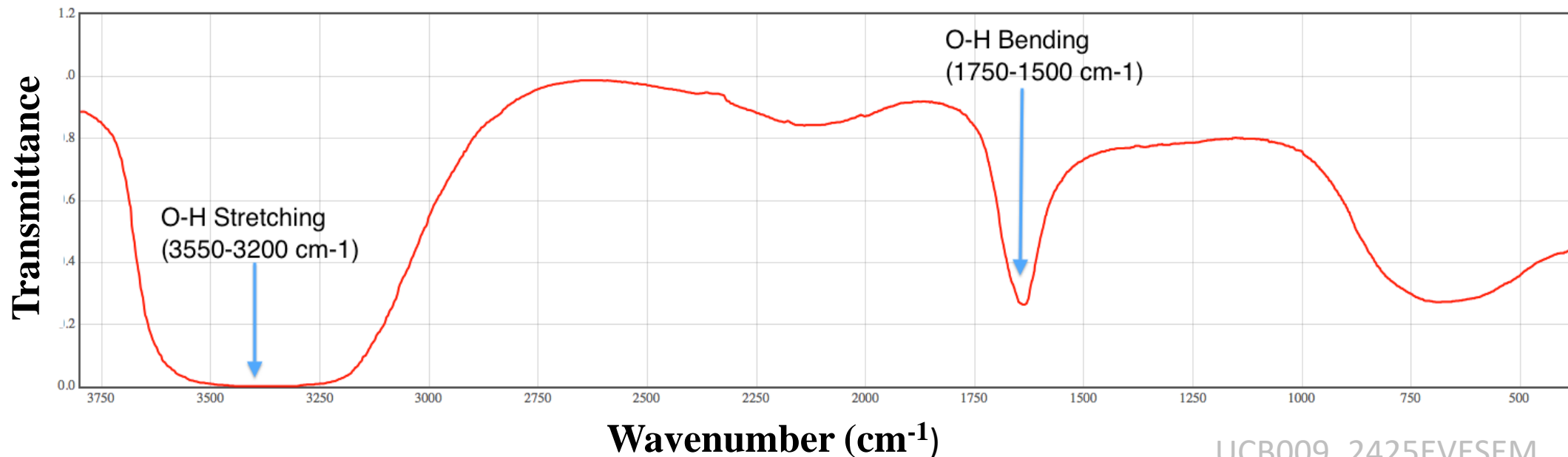
Regions in the IR Spectrum:

IR spectrum of 1-propanol
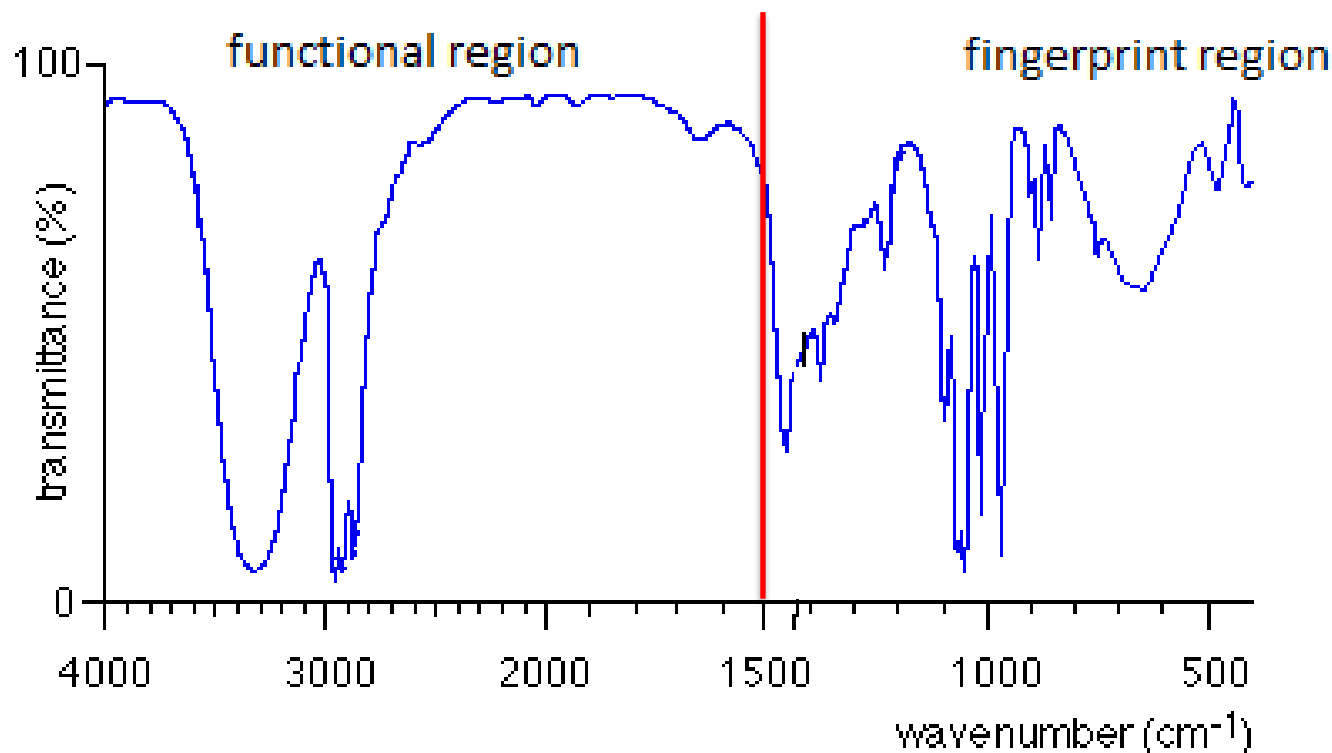
Functional group region or **group frequency** region (**Main focus region**):
- 4000 to 1500 cm^{-1}
- the peaks in this region are usually due to **stretching vibrations.**

Fingerprint region:
- 1500 to 600 cm^{-1}
- the peaks in this region are due to **mostly bending** vibrations and **few stretching** vibrations.

Interpretation of IR Spectrum
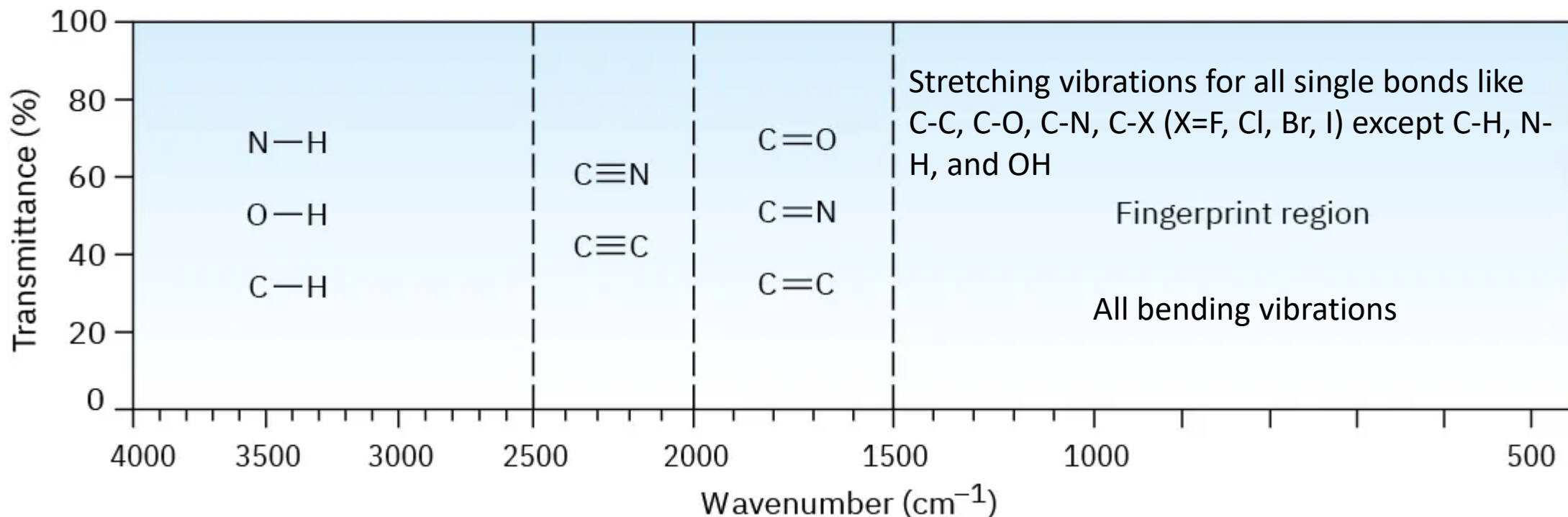
Exercise 9:

Find the approximate range of IR bands that will be observed in the following molecules:
i)   Methanol
ii) Aniline
iii) Acetaldehyde

Hints to solve this exercise:

- Draw the structures of the molecules
- Identify various bonds and the functional groups present in the molecules
- Refer to the IR spectrum given above

Why the Fingerprint Region is Important in IR Spectrum

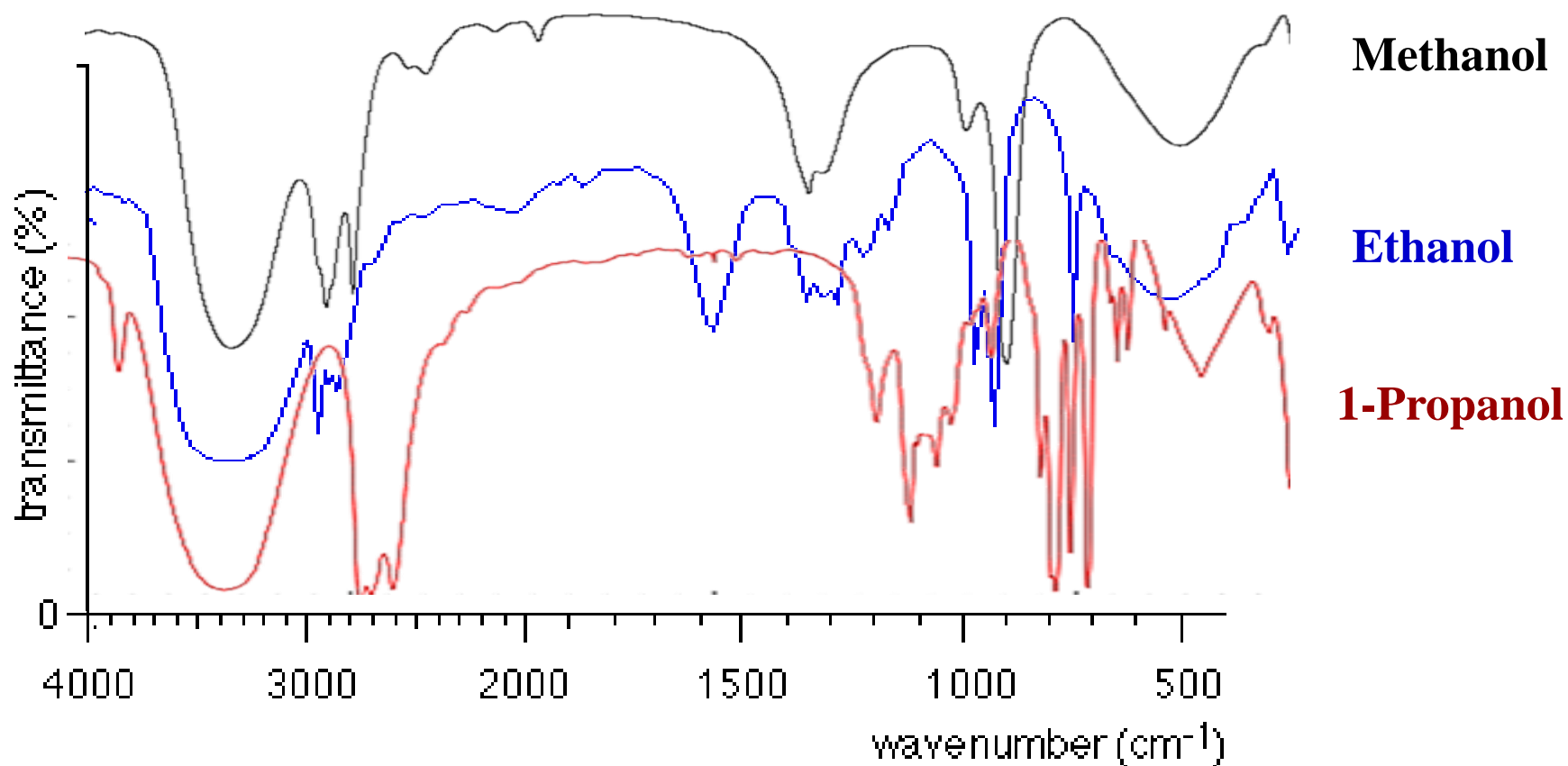Although the **fingerprint region (1500 to 600 cm^{-1})** does not help us in identification of the functional group(s) but it mainly helps us to distinguish between molecules having the same functional group(s)

Methanol

Ethanol

1-Propanol

Since all the samples contain –OH as functional groups, the peaks of –OH stretching mode appear at the same position. However, there are fine differences in the fingerprint region due to additional complex vibrations arising from extra –CH_2 groups present in ethanol and propanol.

Note: If two samples are giving the same spectra in the fingerprint region, then they possess same structures or they are enantiomers

Why does the OH band appear as a broad peak compared to others?

O-H Stretching Mode in IR Spectrum: Effect of Hydrogen Bonding

Pure samples and concentrated solutions of alcohols and phenols show broad O-H stretching bands in the region about 3200-3600 cm^{-1} due to intermolecular hydrogen bonding.

Sharp, non-hydrogen-bonded O-H bands are observed only in the vapor phase, in very dilute solutions, in non-polar solvents, or when hydrogen bonding is prevented by steric hindrance

1-hexanol $CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-OH$
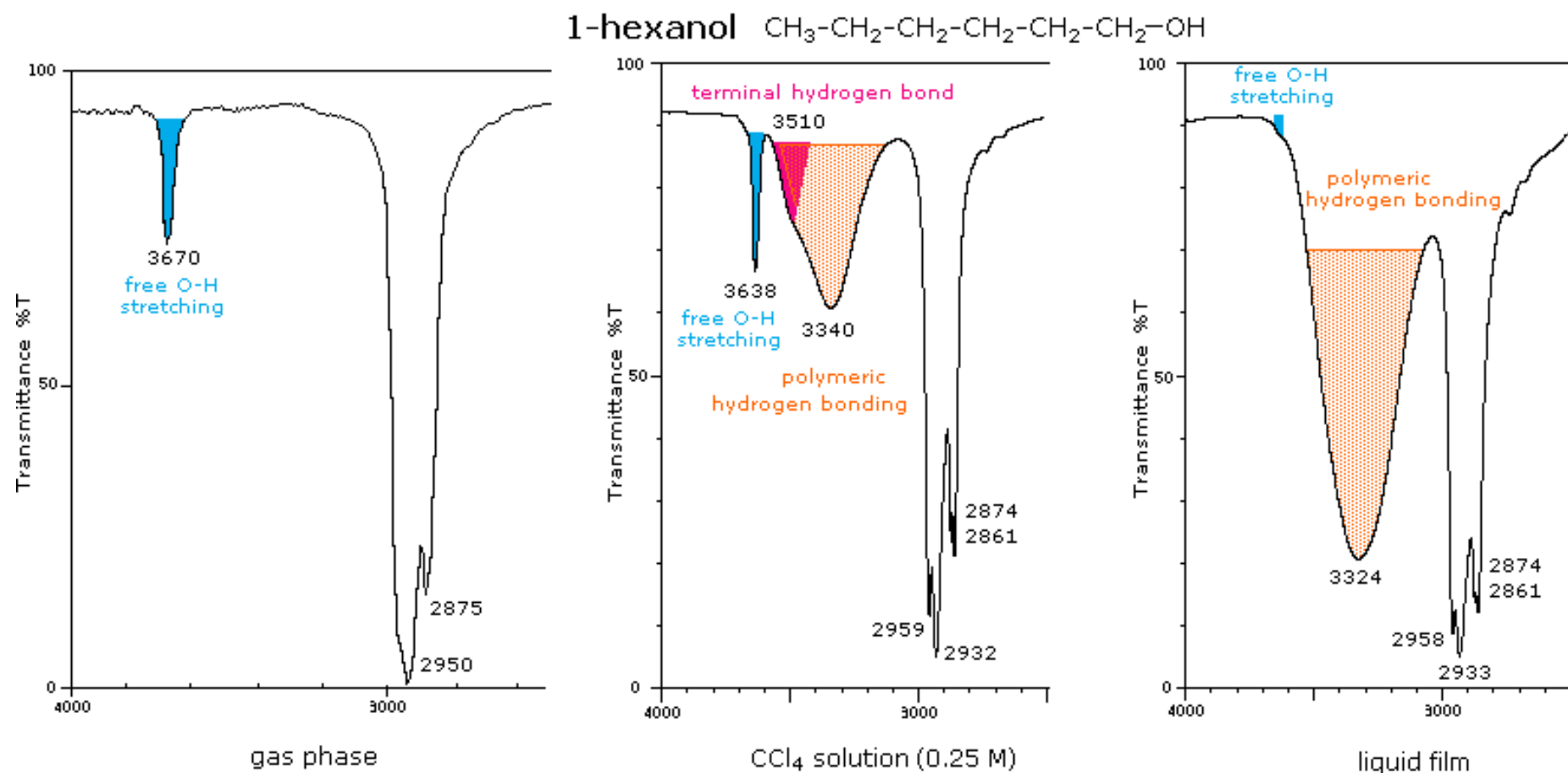
How to distinguish between intramolecular and intermolecular hydrogen bonding, present in molecules, using IR Spectroscopy
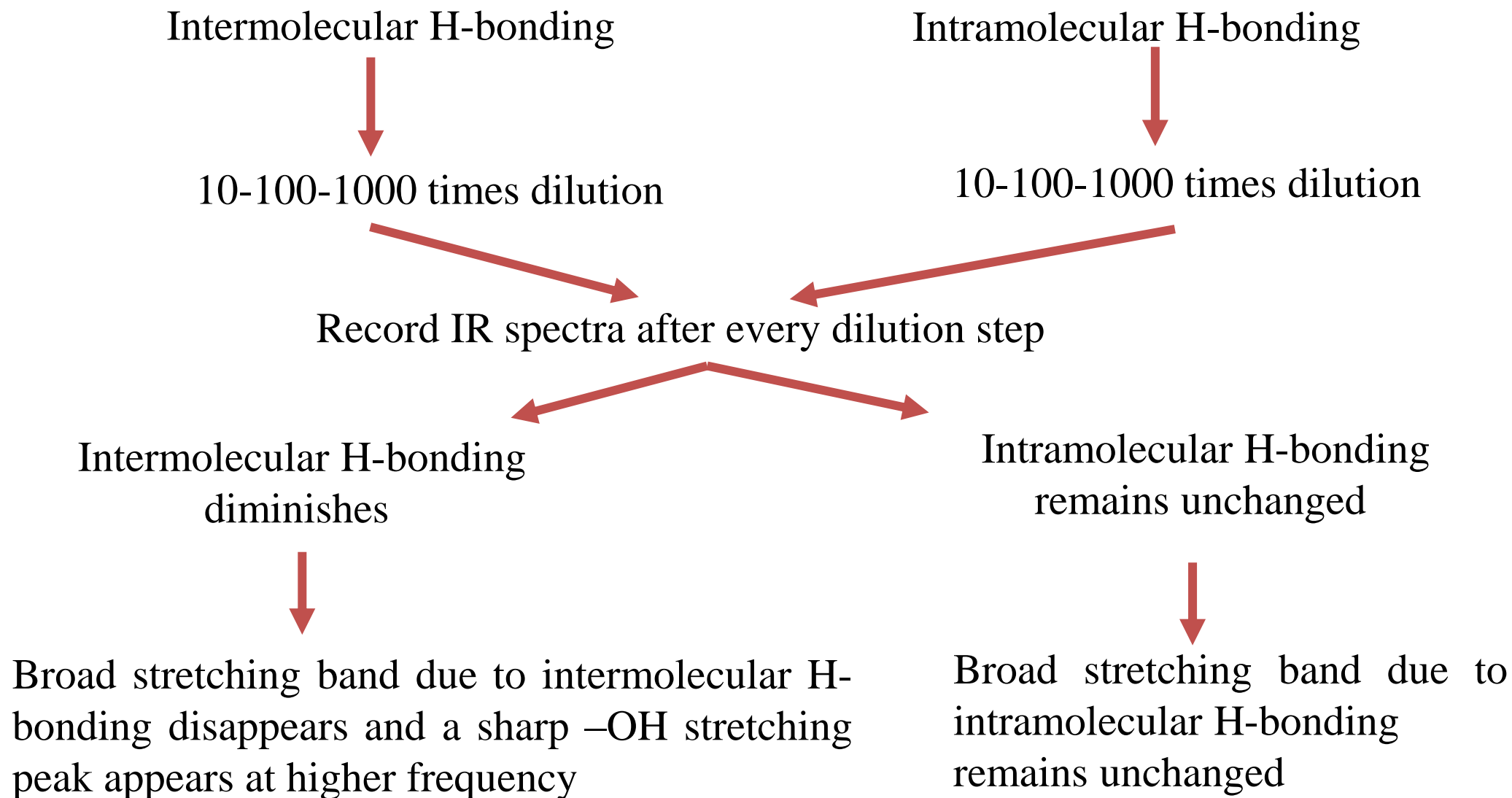
Intermolecular H-bonding

Intramolecular H-bonding

↓

↓

10-100-1000 times dilution

10-100-1000 times dilution

Record IR spectra after every dilution step

Intermolecular H-bonding diminishes

Intramolecular H-bonding remains unchanged

↓

↓

Broad stretching band due to intermolecular H-bonding disappears and a sharp –OH stretching peak appears at higher frequency

Broad stretching band due to intramolecular H-bonding remains unchanged

Note: Dilution is carried out using any non-hydrogen bonding solvent, e.g., carbon tetrachloride (CCl_4).

Effect of Dilution on O-H Stretching Bands in IR spectrum
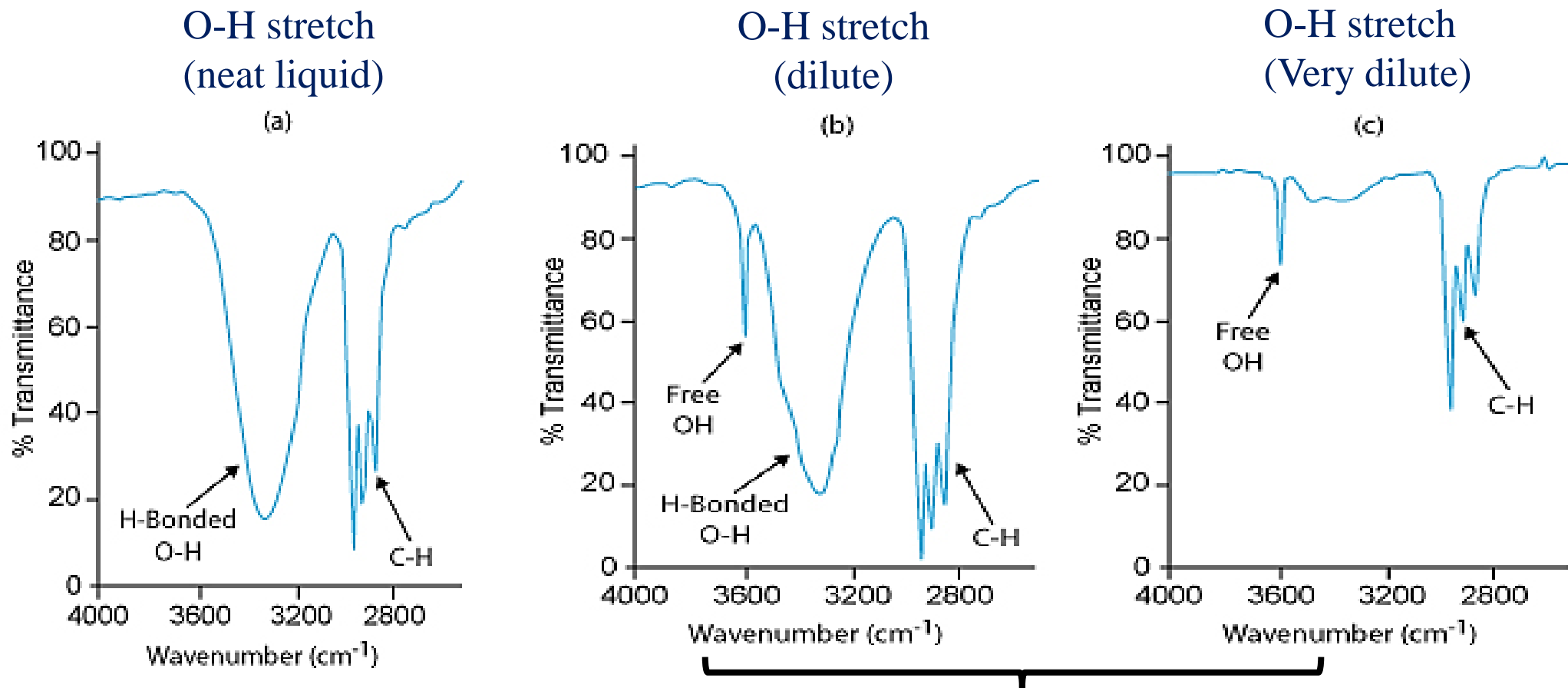
O-H stretch (neat liquid)

O-H stretch (dilute)

O-H stretch (Very dilute)

O-H stretch (Free & hydrogen-bonded)

Note: Dilution is carried out using any non hydrogen bonding solvent e.g. carbon tetrachloride (CCl$_4$) etc.

Since there is change in the shape of hydrogen band in above spectrum so there is intermolecular hydrogen bonding, if there is no change on dilution means molecule has intramolecular hydrogen bonding.

Applications of IR Spectroscopy

- Structural characterization of molecules: Identification of various functional groups.

- It can distinguish between intra and intermolecular hydrogen bonding.

- In detecting impurities: IR spectra of an impure sample show some extra absorption bands. By comparing it with the IR spectra of a pure compound, the presence of impurities can be detected.

- IR spectra provide valuable information on molecular symmetry, dipole moment, bond lengths, etc.